

## Molecular Aggregation in Liquid Dimethylformamide: Raman Spectra and Quantum-Chemical Calculations

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The maximum frequencies of the parallel and perpendicular polarized components of the C=O vibrational band for dimethylformamide (DMF) in Raman spectra differ by  $14.5\text{ cm}^{-1}$ . This difference decreases significantly upon dilution in  $\text{CCl}_4$  and dimethylsulfoxide. The doublet structure of the band is observed in solutions with  $\text{CCl}_4$  in the 0.2 mol fraction concentration region. The above mentioned coincidence of C=O vibration band frequencies in the pure liquid is explained by the complexity of the band, i.e. the presence within the band of two overlapping lines with different values of the depolarization ratio belonging to monomeric molecules (high-frequency) and aggregated forms. In very dilute mixtures, there remain only monomeric molecules and the band acquires a simple shape of a separate line, and the above-mentioned frequency difference vanishes. The quantum-chemical calculations of the optimized structure for the isolated DMF monomer and the dimer show that a dimer structure with nearly zero dipole moment and with two hydrogen bonds (closed dimer) is energetically favorable. In addition, such closed dimer structures correspond to the lower frequency and value of the depolarization ratio than for monomer in Raman spectra of the C=O vibrations. In the liquid state of DMF, the tendency for dimer formation is strong. The calculations are in good agreement with the experimentally observed peculiarities of the DMF C=O vibrational band.